

PREMIUM TRANSPORTATION FUELS FROM SYNGAS. G. Alex Mills, Department of Energy, A-118, Germantown, Washington, D.C. 20545

There is an essential need for synthetic liquid transportation fuels. Indirect liquefaction involving coal derived syngas has gained new interest because of new discoveries in the catalytic synthesis of liquids from  $\text{CO} + \text{H}_2$ . Catalytic improvements have been made in the manufacture of  $\text{CH}_3\text{OH}$  and higher alcohols. Also, higher engine efficiency is made possible by a combination of high compression ratio and catalytic decomposition of alcohol to provide a gaseous fuel to the engine using heat otherwise wasted.

Conversion of  $\text{CH}_3\text{OH}$  over ZSM-5 zeolite catalyst to high octane gasoline is remarkable. Also, beginning with  $\text{CO} + \text{H}_2$  mixtures, of special interest is the application of catalysts having dual functions (metal + acid) in combination with shape selective zeolites for control of both chemical composition and product molecular size. Further, the addition of a shift function to the hydrocarbon synthesis function makes possible the water gas shift in-situ in the reactor, thus permitting the use of syngas of low  $\text{H}_2/\text{CO}$  ratios, although with problems in simultaneous optimization of aromatization and shift reactions.

## The Mechanism of Carbon Oxidation

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Oxidation of single crystal graphite is being studied with the technique of etch-decoration and transmission electron microscopy, which was developed by Hennig et al. and Thomas et al. On the basal or (0001) plane, the carbon atoms surrounding the vacancy are the active sites, which are to be gasified and a circular pit is developed. Two sets of results have been obtained: (a) the rate of C removal per active site depends directly on the population density of the active sites; and (b) for low active-site densities, C removal continues for a prolonged period of time after  $O_2$  is cut off from the gas phase.

Hundreds of crystals have been studied, which contained vacancies from 0.1 to 60 per  $\mu m^2$ . The turnover frequency decreases with increasing vacancy density and levels off at a high density. For example, at 650°C and 0.2 atm  $O_2$  (in Ar), the rate is 0.9 C/C/s for a vacancy density of  $1/\mu m^2$ ; 0.6 C/C/s for  $10/\mu m^2$ ; and levels off at about 0.5 C/C/s.

In the argon purge experiments, rates are measured during the purge after 10 min. of reaction with  $O_2$ . The pit size is more than doubled during argon purge for surfaces with small vacancy densities, whereas no gasification occurs during argon purge with high vacancy densities.

Gasification of C on the edge sites with  $O_2$  involves two independent processes: (a) direct collision by  $O_2$  from gas phase (which follows the Langmuir-Hinshelwood mechanism), and (b) reaction with oxides which are chemisorbed on the basal sites and subsequently migrate to the active sites. Preliminary calculations indicate that the amount of chemisorbed oxide is 0.4 O per basal carbon for the surfaces with low vacancy densities, and that the surface diffusion coefficient is on the order of  $10^{-11}$  cm<sup>2</sup>/s, both at 650°C.

## Catalysis in Coal Liquefaction

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Efficient catalysts, useful at a level less than 1%, can play an important role in the primary liquefaction of coal. Most of our present knowledge of efficient catalysts derives from empirical catalyst screening performed decades ago. By contrast, our understanding of the organic chemistry of coal is advancing at an exponential rate. This understanding will permit formulation of reaction mechanisms that are more soundly based than the ad hoc mechanisms suggested in the past. Still to be tackled is the question of determining the precise role of multifunctional, efficient catalysts in the many reaction steps that occur during coal liquefaction. This paper presents an eclectic consideration of catalyst systems involving tin, molybdenum, or iron which are known to be effective in coal liquefaction in small concentration. Some of the topics to be discussed are the importance of catalyst distribution, the fate of catalyst components during liquefaction, and the chemical role played by the catalyst in accelerating the reactions occurring in liquefaction. The last problem is the least understood and presents the greatest challenge for future research.